

METHOD FOR MANUFACTURING SHALLOW TRENCH  
ISOLATION IN SEMICONDUCTOR DEVICE

Field of the Invention

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The present invention relates to a method for manufacturing a semiconductor device; and, more particularly, to a method for manufacturing a shallow trench isolation (STI) for use in a highly integrated semiconductor device with an enhanced gap-fill property and simultaneously, without a detrimental impact of fluorine by employing a two-stage thermal process.

Description of the Prior Art

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As is well known, in a semiconductor device, there is formed an isolation region for electrically isolating elements from each other. In order to form the isolation region, various techniques have been employed such as a local oxidation of silicon (LOCOS) which uses a thermal oxide or a shallow trench isolation (STI) technique which is suitable for a highly integrated semiconductor device.

The LOCOS technique, however, has several drawbacks that a field oxide (FOX) is deteriorated with a decrease of a design rule and further, a bird's beak structure encroached into an active area of the device. Thus, the LOCOS technique is rarely employed to form the isolation region as the device

becomes micro-miniaturized in nowadays.

To overcome the disadvantage of the LOCOS technique, the STI has been popularly used for a nano-miniaturized device. That is, as the device becomes micro-miniaturized, an effective area of the active region is also reduced by degrees. Therefore, in order to fill the trench having a high aspect ratio with an insulating material, a high density plasma (HDP) oxide has been greatly utilized because it shows good step coverage. In particular, the HDP oxide is referred to as a helium (He)-based HDP oxide because the HDP oxide is formed conventionally by using a source gas including a silane ( $\text{SiH}_4$ ) gas, an oxygen ( $\text{O}_2$ ) gas and a helium (He) gas. However, there is still a limitation to apply the conventional He-based HDP oxide for forming the STI in the micro-miniaturized semiconductor device.

That is, in the STI process for use in an 80 nm scale nano-device, the minimum aspect ratio for securing a trench gap-fill is about 5 but the He-based HDP oxide can be used for forming the trench having only the aspect ratio below about 4. Therefore, in case of using the He-based HDP oxide for the STI, there are inevitably happened micro-voids therein.

In attempt to overcome this limitation of the He-based HDP oxide, there is proposed a method for forming the HDP oxide by flowing a nitrogen trifluoride ( $\text{NF}_3$ ) into the exemplary source gas of  $\text{SiH}_4$  gas,  $\text{O}_2$  gas and He gas, which is carried out through three steps. Among the steps, a first and a second steps are very important steps for filling the HDP

oxide uniformly into the trench without any void therein.

Referring to Figs. 1A to 1C, there are provided cross sectional views setting forth a conventional method for manufacturing the STI by using an  $\text{NF}_3$ -based HDP oxide.

5 In Fig. 1A, a process for manufacturing the STI begins with preparing a semiconductor substrate 110 obtained by a predetermined process. Afterward, a pad oxide layer and a pad nitride layer are formed on the semiconductor substrate 110 in sequence. Then, photoresist masks (not shown) are formed on  
10 predetermined locations of a top face of the pad nitride layer. Thereafter, the pad nitride layer and the pad oxide layer are patterned into a first predetermined configuration by using the photoresist masks as mask patterns till a top face of the semiconductor substrate 110 is exposed, thereby  
15 forming a pad oxide 112 and a pad nitride 114 on the semiconductor substrate 110. Subsequently, the photoresist masks are removed by using a typical method such a photostrip process or the like.

Following the removal of the photoresist masks, the  
20 semiconductor substrate 110 is patterned into a second predetermined configuration by using the pad nitride 114 as an etch mask so as to form a trench structure therein. Afterward, a sidewall oxide layer (not shown) is formed on sidewalls of the trench structure for compensating damage  
25 produced during above etching process and removing dangling bonds existing in the trench structure.

In a subsequent step, a liner nitride 116 is formed over

the resultant structure. Herein, the liner nitride 116 plays a role in reducing stress concentrated into edges and the sidewalls of the trench structure and also preventing the sidewalls of the trench structure from being oxidized during a post oxidation process.

Thereafter, a liner oxide 118 is formed on the liner nitride 116 for preventing the liner nitride 116 from being lifted up due to an excessive stress incurred during a post process for filling the trench structure with an insulating material.

After forming the liner oxide 118, a first high density plasma (HDP) oxide layer, i.e., a hydrogen ( $H_2$ )-based HDP oxide layer 120, is deposited on the liner oxide 118 with a predetermined thickness. That is, the  $H_2$ -based HDP oxide layer 120 is formed by adding  $H_2$  gas to an exemplary source gas of  $SiH_4$  gas,  $O_2$  gas and He gas for improving a step coverage.

Following the formation of the  $H_2$ -based HDP oxide layer 120, a second HDP oxide layer, i.e., a  $NF_3$ -based HDP oxide layer 122 is formed partially in the trench structure and partially on the  $H_2$ -based HDP oxide layer 120 over the pad nitride 114. The  $NF_3$ -based HDP oxide layer 122 is formed by adding  $NF_3$  gas to the exemplary source gas of  $SiH_4$  gas,  $O_2$  gas and He gas, for providing a good gap-fill property. Since the  $NF_3$  gas serves as a chemical etchant during the deposition process, it is possible to prevent an unnecessary deposition on the sidewalls of the trench such as a re-deposition

phenomenon during a sputtering process. Moreover, the  $\text{NF}_3$ -based HDP oxide layer 122 is thickly formed on the bottom of the trench structure as the deposition process is performed more and more. On the contrary, the  $\text{NF}_3$ -based HDP oxide layer 122 is rarely formed on the sidewalls of the trench structure. Therefore, the  $\text{NF}_3$ -based HDP oxide layer 122 can be uniformly formed into the trench structure having a high aspect ratio without micro-voids therein, thereby securing a good gap-fill property.

Referring to Fig. 1C, after the formation of the  $\text{NF}_3$ -based HDP oxide layer 122, the He-based HDP oxide layer 124 is deposited over the resultant structure by using an exemplary source gas of  $\text{SiH}_4$  gas,  $\text{O}_2$  gas and He gas. Thereafter, the He-based HDP oxide layer 124 is planarized by using a method such as a chemical mechanical polishing (CMP) or the like. After removing the pad nitride 114, the conventional method for manufacturing the STI is completed.

According to the conventional method, it provides a good gap-fill property when the HDP oxide is formed by using the source gas containing  $\text{NF}_3$  gas. But, since there exists a fluorine (F) in the  $\text{NF}_3$ -based HDP oxide layer 122, the fluorine has a detrimental effect on a gate oxide during a post thermal process. Therefore, it is difficult to expect a reliable semiconductor device in the long run.

## Summary of the Invention

It is, therefore, an object of the present invention to provide a method for manufacturing a shallow trench isolation (STI) in a semiconductor device with an enhanced gap-fill property and without a detrimental effect of fluorine by employing a two-stage thermal process.

In accordance with one aspect of the present invention, there is provided a method for manufacturing an STI in a semiconductor device, the method including the steps of: a) preparing a semiconductor substrate obtained by a predetermined process on which a pad oxide and a pad nitride are formed on predetermined locations thereof; b) forming a trench structure in the semiconductor substrate; c) forming a hydrogen ( $H_2$ )-based high density plasma (HDP) oxide layer over a first resultant structure; d) forming a nitrogen trifluoride ( $NF_3$ )-based HDP oxide layer into the trench structure with a predetermined depth; e) carrying out a two-stage thermal process for removing fluorine in the  $NF_3$ -based HDP oxide layer; and f) forming a helium (He)-based HDP oxide layer over a second resultant structure.

In accordance with another aspect of the present invention, there is provided a method for manufacturing an STI in a semiconductor device, the method including the steps of: a) preparing a semiconductor substrate obtained by a predetermined process on which a pad oxide and a pad nitride are formed on predetermined locations thereof; b) forming a

trench structure in the semiconductor substrate; c) forming a hydrogen ( $H_2$ )-based high density plasma (HDP) oxide layer over a first resultant structure; d) forming a nitrogen trifluoride ( $NF_3$ )-based HDP oxide layer into the trench structure with a predetermined depth; e) forming a helium (He)-based HDP oxide layer over a second resultant structure; and f) carrying out a two-stage thermal process for removing fluorine in the  $NF_3$ -based HDP oxide layer.

#### Brief Description of the Drawings

The above and other objects and features of the present invention will become apparent from the following description of the preferred embodiments given in conjunction with the accompanying drawings, in which:

Figs. 1A to 1C are cross sectional views setting forth a conventional method for manufacturing a shallow trench isolation (STI) in a semiconductor device;

Figs. 2A to 2D are cross sectional views illustrating a method for manufacturing an STI in a semiconductor device in accordance with a preferred embodiment of the present invention; and

Figs. 3A and 3B are cross sectional views depicting states of covalent bonds of silicon existing in each layer formed before and after carrying out a two-stage thermal process in accordance with the preferred embodiment of the present invention.

## Detailed Description of the Preferred Embodiments

There are provided in Figs. 2A to 2C and Figs. 3A and 3B cross sectional views setting forth a method for manufacturing a shallow trench isolation (STI) in a semiconductor device in accordance with a preferred embodiment of the present invention. It should be noted that like parts appearing in Figs. 2A to 2C and Figs. 3A and 3B are represented by like reference numerals.

Referring to Fig. 2A, a process for manufacturing the STI in the semiconductor device begins with preparing a semiconductor substrate 210 obtained by a predetermined process. Afterward, a pad oxide layer and a pad nitride layer are formed on the semiconductor substrate 210 in sequence. Then, photoresist masks (not shown) are formed on predetermined locations of a top face of the pad nitride layer. Thereafter, the pad nitride layer and the pad oxide layer are patterned into a first predetermined configuration by using the photoresist masks as mask patterns till a top face of the semiconductor substrate 210 is exposed, thereby forming a pad oxide 212 and a pad nitride 214 on the semiconductor substrate 210. Subsequently, the photoresist masks are removed by using a typical method such a photostrip process.

Following the removal of the photoresist masks, the semiconductor substrate 210 is patterned into a second predetermined configuration by using the pad nitride 214 as an



etch mask so as to form a trench structure therein. Afterward, a sidewall oxide layer (not shown) is formed on sidewalls of the trench structure for compensating damage produced during above etching process and removing dangling  
5 bonds existing in the trench structure.

In a subsequent step, a liner nitride 216 is formed over the resultant structure. Herein, the liner nitride 216 plays a role in reducing a stress concentrated into edges and the sidewalls of the trench structure and also preventing the  
10 sidewalls of the trench structure from being oxidized during a post oxidation process.

Thereafter, a liner oxide 218 is formed on the liner nitride 216 for preventing the liner nitride 216 from being lifted up due to an excessive stress incurred during a post  
15 process for filling the trench structure with an insulating material.

After forming the liner oxide 218, a first high density plasma (HDP) oxide layer, i.e., a hydrogen ( $H_2$ )-based HDP oxide layer 220, is deposited on the liner oxide 218 with a  
20 predetermined thickness. That is, the  $H_2$ -based HDP oxide layer 220 is formed by adding  $H_2$  gas to an exemplary source gas for use in a conventional method for depositing a helium (He)-based HDP oxide layer, wherein the exemplary sources gas includes silane ( $SiH_4$ ) gas, oxygen ( $O_2$ ) gas and He gas.  
25 Herein, the purpose of adding  $H_2$  gas to the exemplary source gas is to enhance a step coverage of the device. It is preferable that a flow rate of  $SiH_4$  gas,  $O_2$  gas, He gas and  $H_2$

gas should be in the range of about 40 sccm to about 50 sccm,  
of about 50 sccm to about 60 sccm, of about 400 sccm to about  
600 sccm and of about 50 sccm to about 150 sccm, respectively.  
Thus, it is possible to improve the step coverage while  
5 maintaining a low deposition rate. It is noted that the above  
flow rate should be determined in consideration of a trench  
profile, a critical dimension of a space, a depth of the  
trench and so forth.

In order to maintain the low deposition rate during the  
10 formation of the H<sub>2</sub>-based HDP oxide layer 220, a low frequency  
(LF) power is supplied in the range of about 3,000 W to about  
3,500 W and a high frequency (HF) power is supplied in the  
range of about 400 W to about 600 W.

Following the formation of the H<sub>2</sub>-based HDP oxide layer  
15 220, a second HDP oxide layer, i.e., a nitrogen trifluoride  
(NF<sub>3</sub>)-based HDP oxide layer 222 is formed partially in the  
trench structure and partially on the H<sub>2</sub>-based oxide layer 220  
over the pad nitride 214. Herein, the NF<sub>3</sub>-based HDP oxide  
layer 222 is formed by adding NF<sub>3</sub> gas to the exemplary source  
20 gas of SiH<sub>4</sub> gas, O<sub>2</sub> gas and He gas, for securing a good gap-  
fill property. It is important that the deposition process of  
the NF<sub>3</sub>-based HDP oxide layer 222 should be carried out to  
maximize the deposition rate in a bottom area of the trench  
and to minimize the deposition rate in the sidewalls of the  
25 trench. Thus, in order to satisfy the above conditions, it is  
preferable that the flow rate of SiH<sub>4</sub> gas, O<sub>2</sub> gas, He gas and  
NF<sub>3</sub> gas should be in the range of about 50 sccm to about 70

sccm, of about 100 sccm to about 150 sccm, of about 40 sccm to about 60 sccm and of about 20 sccm to about 80 sccm, respectively. Furthermore, it is preferable that the LF power should be supplied in the range of about 4,000 W to about 6,000 W and the HF power should be supplied in the range of about 900 W to about 1,000 W.

Since the  $\text{NF}_3$  gas serves as a chemical etchant during the deposition process, it is possible to prevent an unnecessary deposition on the sidewalls of the trench such as a re-deposition phenomenon during a sputtering process. Moreover, the  $\text{NF}_3$ -based HDP oxide layer 222 is thickly formed on the bottom of the trench as the deposition process is performed more and more. On the contrary, the  $\text{NF}_3$ -based HDP oxide layer 222 is rarely formed on the sidewalls of the trench. Therefore, the  $\text{NF}_3$ -based HDP oxide layer 222 can be uniformly formed in the trench structure having a high aspect ratio without micro-voids therein. Herein, it is noted that a top surface of the  $\text{NF}_3$ -based HDP oxide layer 222 should be lower than that of the trench structure for preventing the  $\text{NF}_3$ -based HDP oxide layer 222 from being exposed after a chemical mechanical polishing (CMP) or a cleaning process. Although a concentration of fluorine (F) in the  $\text{NF}_3$ -based HDP oxide layer 222 is smaller than that of fluorine in a fluorine-doped silicate glass (FSG) which is commonly used for an interlayer dielectric, fluorine in the  $\text{NF}_3$ -based HDP oxide layer 222 still has a detrimental effect on a gate oxide in a post process.

In order to remove fluorine in the  $\text{NF}_3$ -based HDP oxide layer 222 in the present invention, therefore, a two-stage thermal process is carried out. A detailed description of carrying out the two-stage thermal process will be illustrated hereinafter.

Referring to Figs. 3A and 3B, there are schematic cross sectional views setting forth depicting states of covalent bonds of silicon existing in each layer formed before and after carrying out a two-stage thermal process in accordance with the preferred embodiment of the present invention.

In Fig. 3A, there are shown representative covalent bonds of silicon existing in the layers before carrying out the two-stage thermal process. It is understood that whole the layers except the  $\text{NF}_3$ -based HDP oxide layer 222 has mainly Si-O covalent bond but the  $\text{NF}_3$ -based HDP oxide layer 222 has Si-F covalent bond therein. The fluorine in Si-F covalent bond is dissociated during a post thermal process so that fluorine may diffuse into the gate oxide. In the result, the gate oxide may be deteriorated at last as describe already.

To overcome the above problem, referring to Fig. 2B, a first-stage thermal process is carried out in  $\text{H}_2\text{O}$  ambient for about 30 minutes to about 10 hours at a temperature ranging from about  $700^\circ\text{C}$  to about  $1,100^\circ\text{C}$  in a diffusion furnace. During the first-stage thermal process,  $\text{H}_2\text{O}$  molecules are penetrated into the  $\text{NF}_3$ -based HDP oxide layer 222 so that the  $\text{H}_2\text{O}$  molecules react with Si-F covalent bond. This chemical reaction results in producing Si-OH bond and gaseous state of



based HDP oxide layer 224. In this case, the aforementioned results are also achieved.

Referring to Fig. 2D, after the formation of the  $\text{NF}_3$ -based HDP oxide layer 222, the He-based HDP oxide layer 224 is deposited over the resultant structure by using the exemplary source gas of  $\text{SiH}_4$  gas,  $\text{O}_2$  gas and He gas. In forming the He-based HDP oxide layer 224, it is preferable that the flow rate of  $\text{SiH}_4$  gas,  $\text{O}_2$  gas and He gas should be in the range of about 150 sccm to about 250 sccm, of about 300 sccm to about 400 sccm and of about 400 sccm to about 600 sccm, respectively. The He-based HDP oxide layer 224 is conventionally used for forming the trench isolation. Accordingly, it is unnecessary to modify the post CMP process and the post cleaning process in the present invention. Since the process for forming the He-based HDP oxide layer 224 is well known to those in the art, further detail descriptions will be abbreviated herein.

As described above, the inventive method for forming the STI in the semiconductor device employs the two-stage thermal process of which the first-stage thermal process is carried out in  $\text{H}_2\text{O}$  ambient and the second-stage thermal process is carried out in  $\text{N}_2$  gas ambient. Therefore, the inventive method can be applied to the semiconductor device with a design rule of below 80 nm because it ensures the device with an enhanced gap-fill property and without the detrimental effect of fluorine.

While the present invention has been described with respect to the particular embodiments, it will be apparent to

those skilled in the art that various changes and modifications may be made without departing from the scope of the invention as defined in the following claims.